

**METHODS AND COMPOSITIONS FOR SEALING PIPE  
AND FORMING BARRIERS IN WELL BORES**

**BACKGROUND OF THE INVENTION**

**1. FIELD OF THE INVENTION**

**[0001]** The present invention relates generally to methods and compositions for forming barriers in well bores such as barriers in the annulus between a casing, liner or screen and the walls of a well bore.

**2. DESCRIPTION OF THE PRIOR ART**

**[0002]** In the completion of well bores penetrating subterranean producing zones, casings or liners are often sealed therein to prevent the inflow or outflow of fluids. The sealing composition utilized has generally been a cement composition having a relatively high density. The high density requires the use of special cement composition pumping equipment which is costly to obtain and use to pump the cement composition into the annulus between the casing or liner and the walls of the well bore. Also, the high density of the cement composition increases the well head pressure during pumping which can and often does form undesirable fractures in the walls of the well bore.

**[0003]** A well completion operation often conducted in the portion of a well bore penetrating a subterranean producing zone is gravel packing. In gravel packing operations, particles referred to in the art as gravel are carried to the subterranean producing zone in which a gravel pack is to be placed by hydrocarbon or water carrying fluids. Prior to placing the gravel particles in the subterranean zone, a screen is often placed in the subterranean zone for retaining the gravel particles in the zone. After the

screen is placed in the zone, the gravel particles are pumped into the zone between the walls of the well bore and the screen therein. Once the particles are placed in the zone, the treating fluid leaks off into the zone and/or it is returned to the surface. The gravel pack produced functions as a filter to separate formation solids from produced fluids while permitting the produced fluids to flow into and through the well bore.

[0004] After a subterranean producing zone has been gravel packed and produced, it is often necessary to isolate one or more portions of the producing zone to prevent the inflow of undesirable fluids such as salt water using a hardenable, low density sealing composition. While hardenable low density sealing compositions have been developed and used heretofore, there are continuing needs for improved hardenable, low density sealing compositions for sealing pipe or forming annular barriers in well bores. In addition, there are needs for such sealing compositions that can be placed into a gravel pack by directly injecting the hardenable, low density sealing compositions through gravel pack screens or expandable screens.

#### SUMMARY OF THE INVENTION

[0005] By the present invention improved methods and compositions for sealing pipe and forming barriers in well bores are provided which meet the needs described above and overcome the shortcomings of the prior art. The hardenable, low density sealing compositions of this invention are furan sealant compositions which are very resistant to chemicals and high temperature environments. The furan sealing compositions also provide greatly superior and longer lasting seals between well bores and strings of pipe as well as for forming barriers in well bores than the sealing compositions used heretofore.

[0006] The sealing compositions of this invention are basically comprised of a hardenable furan liquid resin mixture, an organosilane coupling agent, a cationic surfactant, and hollow microspheres. The sealing compositions can also optionally include a solvent or diluent, a dispersing agent, and a light weight filler.

[0007] The methods of this invention for sealing pipe or forming a barrier in a well bore are comprised of the following steps. A hardenable, low density sealing composition is prepared comprising a hardenable furan liquid resin mixture, an organosilane coupling agent, a cationic surfactant, and hollow microspheres. The sealing composition is placed in a well bore and then allowed to harden into an impermeable mass.

[0008] The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

[0009] The hardenable, low density sealing compositions of this invention basically comprise a hardenable furan liquid resin mixture, an organosilane coupling agent, a cationic surfactant, and hollow microspheres.

[0010] Furan resin can withstand high temperatures without deterioration, i.e., temperatures up to about 600°F, and are resistant to contact with harsh chemicals. Furan resin is self-catalyzed and cures at temperatures above about 275°F. At temperatures below about 275°F, a delayed or encapsulated catalyst is utilized to cause the furan resin to cure and harden.

[0011] The hardenable furan liquid resin mixture in the sealing composition of this invention comprises a 2-furanmethanol homopolymer present in the mixture in an

amount in the range of from about 55% to about 60% by weight thereof and furfuryl alcohol present in the mixture in an amount in the range of from about 40% to about 45% by weight thereof. The furan liquid resin mixture is present in the sealing composition in an amount in the range of from about 10% to about 50% by weight thereof, preferably in an amount of about 35%.

[0012] Various solvents or diluents can optionally be used to thin down the resin mixture if necessary to obtain a desirable viscosity and especially when solid particulate fillers are blended in the resin mixture. Examples of solvents or diluents that can be used include, but are not limited to, 2-butoxy ethanol, butyl acetate, furfuryl acetate, or mixtures thereof. Of these, furfuryl acetate is preferred. When used, the solvent or diluent is included in the sealing composition in an amount in the range of from about 5% to about 60% by weight of the sealing composition.

[0013] Examples of organosilane coupling agents that can be utilized in the sealing compositions include, but are not limited to, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and n-beta(aminoethyl)-gamma-aminopropyltrimethoxysilane. Of these, n-beta(aminoethyl)-gamma-aminopropyltrimethoxysilane is preferred. The organosilane coupling agent is included in the sealing composition in an amount in the range of from about 0.1% to about 3% by weight thereof, preferably in an amount of about 1%.

[0014] The cationic surfactant in the sealing composition functions to improve the contact of the furan sealing composition with surfaces of particulate fillers and strengthen the bond of the sealing composition to the surfaces it contacts. Examples of cationic surfactants that can be used include, but are not limited to, ethoxylated nonyl

phenol phosphate ester, C<sub>12</sub>-C<sub>22</sub> alkyl phosphonates, and mixtures of one or more cationic surfactants and one or more non-ionic surfactants. Of these, a C<sub>12</sub>-C<sub>22</sub> alkyl phosphonate surfactant is preferred. The cationic surfactant is present in the sealing composition in an amount in the range of from about 0.1% to about 10% by weight thereof, preferably in an amount of about 5%.

[0015] Examples of dispersing agents that can optionally be utilized in the sealing compositions include, but are not limited to, naphthalene-sulfonate-formaldehyde condensates, acetone-formaldehyde-sulfite condensates and glucano-delta-lactone. Of these, naphthalene-sulfonate-formaldehyde condensates are preferred. When used, the dispersing agent which functions to disperse solids in the sealing composition is generally present in the sealing composition in an amount in the range of from about 0.1% to about 5% by weight thereof, preferably in an amount of about 1%.

[0016] A variety of light weight fillers can optionally be included in the sealing composition including, but not limited to, amorphous silica, fumed silica, diatomaceous earth and fly ash. Of these, amorphous silica is preferred. When used, the light weight filler is present in the sealing composition in an amount in the range of from about 5% to about 50% by weight thereof, preferably in an amount of about 30%.

[0017] The hollow microspheres are included in the sealing compositions of this invention to lower the density of the compositions. A variety of hollow microspheres can be utilized in accordance with this invention including, but not limited to, hollow mineral glass spheres that are commercially available under the trade name "SPHERELITES™" from Halliburton Energy Services of Duncan, Oklahoma; hollow cenospheres formed of silica and alumina filled with low pressure gases commercially

available under the trade designation "CENOLIGHT<sup>®</sup>" from Microspheres, S.A.; hollow microspheres that are formed of glass and are commercially available under the trade designation "SCOTCHLIGHT<sup>™</sup>" from the 3-M Company of St. Paul, Minnesota; and microspheres formed of ceramic material that are commercially available under the trade designation "Z-LIGHT SPHERES<sup>™</sup>" from the 3-M Company of St. Paul, Minnesota. Of these, mineral glass spheres are generally preferred. The hollow microspheres utilized are generally present in the sealing composition in an amount in the range of from about 5% to about 50% by weight thereof.

[0018] The sealing compositions of this invention can also optionally include sand as an additional filler. When used, the sand preferably has a mesh size in the range of from about 70 mesh to about 140 mesh and is present in the sealing composition in an amount in the range of from about 5% to about 30% by weight of the sealing composition.

[0019] As mentioned above, when the temperature to which a sealing composition of this invention is exposed is below about 275°F, the sealing composition includes a delayed catalyst for causing the sealing composition to harden. While a variety of catalysts can be utilized, presently preferred catalysts include, but are not limited to, encapsulated hydrochloric acid, encapsulated maleic acid, encapsulated salicylic acid, encapsulated sodium bisulfate, encapsulated phosphoric acid, and encapsulated sulfonic acid. Of these, encapsulated sulfonic acid is the most preferred. The encapsulated material on the catalysts slowly dissolves or otherwise releases the catalysts over time. When used, the catalyst is present in the sealing composition in an amount in the range of from about 0.1% to about 5% by weight of the composition.

**[0020]** The low density furan sealing compositions of this invention include solid materials of small diameters whereby the compositions can be injected through sand screens and the like to form annular barriers therein. Additionally, the low density furan sealing compositions can be utilized for sealing casing and liners in well bores, for sealing holes and cracks in casing and liners, for sealing voids in the annuluses behind sand control screens or expandable screens, and for plugging fractures and the like in well bores.

**[0021]** The methods of the present invention for sealing pipe or forming a barrier in a well bore basically comprise the following steps. A hardenable, low density sealing composition is prepared or provided comprising a hardenable furan liquid resin mixture, an organosilane coupling agent, a cationic surfactant, and hollow microspheres. The sealing composition is placed in the well bore and then allowed to harden into an impermeable mass therein.

**[0022]** A preferred hardenable, low density sealing composition of this invention comprises: a hardenable furan liquid resin mixture; an organosilane coupling agent; a cationic surfactant; and hollow microspheres.

**[0023]** A preferred method of sealing pipe or forming a barrier in a well bore comprises the steps of: (a) preparing or providing a hardenable, low density sealing composition comprising a hardenable furan liquid resin mixture, an organosilane coupling agent, a cationic surfactant, and hollow microspheres; (b) placing the sealing composition in the well bore; and (c) allowing the sealing composition to harden into an impermeable mass.

**[0024]** In order to further illustrate the methods and compositions of this invention, the following example is given.

## EXAMPLE

[0025] A number of samples of the low density sealant compositions of the present invention were prepared containing furan liquid resin mixtures comprising 55% of 2-furanmethanol by weight and 45% furfuryl alcohol by weight purchased from Durez Corp. of New York. The furan liquid resin mixtures were mixed with butyl acetate diluent or furfuryl acetate diluent and the resulting mixtures were then blended with N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, sodium bisulfate acid catalyst, water for dissolving the acid catalyst, 70/170-mesh sand filler, and hollow microspheres. The samples were then cured at a temperature of 325°F for various cure times. After curing, the compressive strengths of the samples were measured. The amounts of the components in each low density sealant composition sample, the curing times of the samples, and the compressive strengths of the samples are given in Table 1 below.

TABLE 1

Composition	Sample 1	Sample 2	Sample 3	Sample 4
Furan System, mL	20	20	20	20
Butyl Acetate (BA) or Furfuryl Acetate (FA), mL	5 (BA)	5 (BA)	5 (FA)	5 (FA)
Silane coupling agent, mL	0.2	0.2	0.2	0.2
Sodium Bisulfate, grams	1	3	1	3
Water, mL	1	3	1	3
70/170-mesh sand, grams	1	3	1	3
Hollow Microspheres (Z-LIGHT SPHERES™), grams	1	3	1	3
Cure time @325°F, hours	96	96	96	96
Compressive Strength, psi	3609	3504	5915	6218

[0026] Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned, as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

[0027] What is claimed is: